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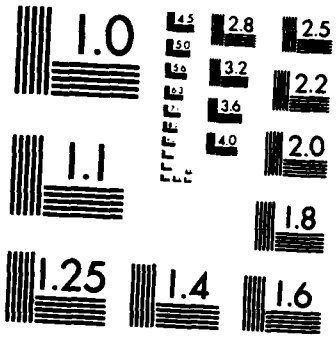


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# ELASTOMERIC POLYSILOXANE MODIFIERS FOR EPOXY NETWORKS. I SYNTHESIS OF FUNCTIONAL OLIGOMERS AND NETWORK FORMATION STUDIES

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Novel elastomeric polysiloxane modifiers for epoxy networks have been synthesized and characterized. In addition, curing studies of conventional epoxy resins incorporating these oligomers have been conducted. Structures were prepared having either epoxide, primary amine and/or secondary amine endgroups. The polymerization step for the siloxanes consisted of a base catalyzed equilibration of the appropriately functionalized disiloxane and octamethylcyclotetrasiloxane. In the case of hydroxy piperazine terminated modifiers, polymers were first synthesized with epoxy endgroups. These endgroups were then subsequently capped with an excess of piperazine prior to curing. The oligomers were characterized by FTIR, $^1H$ and $^{13}C$ NMR, GPC, endgroup analysis and vapor pressure osmometry. The secondary amine terminated oligomers basically act as linear modifiers. By contrast, the aminopropyl functional siloxanes produce a cross-linked network. Piperazine terminated oligomers show much better compatibility with the epoxy resins compared to the aminopropyl terminated oligomers. This is especially true if the modifier contains an amide group. The curing reactions of the epoxy resins (EPON resin-828) using these oligomers and a cyclo-aliphatic diamine (PACM-20) were followed under a variety of conditions by DSC. Percent conversion versus time plots showed that reactivities of the functional siloxanes are higher than the cycloaliphatic amine at comparable temperatures. X-ray photoelectron spectroscopy shows the surfaces of the polysiloxane modified materials to be predominantly siloxane even at quite low bulk levels of the reactive oligomers. Preliminary mechanical property studies are encouraging and detailed morphology-property studies are continuing.

## INTRODUCTION

Epoxy resins are one of the most important classes of thermosetting polymers. They are widely used for many important

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Novel elastomeric polysiloxane modifiers for epoxy networks have been synthesized and characterized. In addition, curing studies of conventional epoxy resins incorporating these oligomers have been conducted. Structures were prepared having either epoxide, primary amine and/or secondary amine endgroups. The polymerization step for the siloxanes consisted of a base catalyzed equilibration of the appropriately functionalized disiloxane and octamethylcyclotetrasiloxane. In the case of hydroxy piperazine terminated

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modifiers, polymers were first synthesized with epoxy endgroups. These endgroups were then subsequently capped with an excess of piperazine prior to curing. The oligomers were characterized by FTIR, $^{1}H$ and $^{13}C$ NMR, GPC, endgroup analysis and vapor pressure osmometry. The secondary amine terminated oligomers basically act as linear modifiers. By contrast, the aminopropyl functional siloxanes produce a crosslinked network. Piperazine terminated oligomers show much better compatibility with the epoxy resins compared to the aminopropyl terminated oligomers. This is especially true if the modifier contains an amide group. The curing reactions of the epoxy resins (EPON resin-828) using these oligomers and a cycloaliphatic diamine (PACM-20) were followed under a variety of conditions by DSC. Percent conversion versus time plots showed that reactivities of the functional siloxanes are higher than the cycloaliphatic amine at comparable temperatures. X-ray photoelectron spectroscopy shows the surfaces of the polysiloxane modified materials to be predominantly siloxane even at quite low bulk levels of the reactive oligomers. Preliminary mechanical property studies are encouraging and detailed morphology-property studies are continuing.

applications such as coatings, adhesives, reinforced plastics and matrix resins for advanced composite materials (1-4). If the network structure is properly generated, epoxy materials can exhibit excellent corrosion and solvent resistance, good adhesion to many substrates and adequate electrical properties. However, in contrast to such desirable characteristics, epoxy networks are typically rather brittle and display rather low fracture toughness. Moreover, the nature of the crosslinking agent and its concentration may also induce relatively high water absorption characteristics. For example, a structural epoxy system may be cured with aromatic amines. The resulting nitrogen containing crosslink provides sites for hydrogen bonding to water. Absorption of water has the effect of plasticizing these materials and thus deteriorating one of their more desirable characteristics. Moreover, the lack of toughness has limited the application characteristics of these systems. Many studies have been conducted which have attempted to improve the fracture and/or impact energies of the networks, while at the same time retaining the other properties. In order to do this, one must closely define the parameters such as the modifier structure, molecular weight, solubility parameter, and concentration of the elastomer. In addition, the structure and reactivity of the hardener and the curing agent must be carefully controlled (5-8). It is important initially to define elastomer systems that are sufficiently "miscible" with the uncured epoxy formulation that they can be adequately dispersed. During the formation of the network (e.g. the curing step), if the solubility parameter of the elastomer and epoxy matrix structure differ sufficiently, it has been possible to develop phase separated elastomer epoxy materials. Thus, small domains of the rubber phase which would be the minority component may be dispersed in the continuous matrix composed of the epoxy resin and the hardener. This dynamic formation of the multiphase structure is very sensitive to reaction conditions and the characteristics of the rubber, such as its molecular weight. Therefore, the functionality and reactivity of the elastomer as compared with the hardener are also important parameters.

Previously, most of the research on the toughening of epoxy networks has utilized the commercially available carboxy terminated butadiene-acrylonitrile (NBR) rubbers (6, 9-11). The carboxy materials are capable of interacting with the epoxy groups to generate a hydroxyester as shown in Scheme 1. Thus, this route has provided a mechanism for chemically bonding the elastomeric component to the rigid matrix. The chemically bonded system then presumably should provide a relatively stable linkage between the modifier and the matrix. If the rubber particles are of appropriate size, they may modify the properties of the epoxy system in a somewhat analogous way to the toughening of thermoplastics (23). It is thought, for example, that the mechanism of craze yielding may be influenced by the presence of the elastomer

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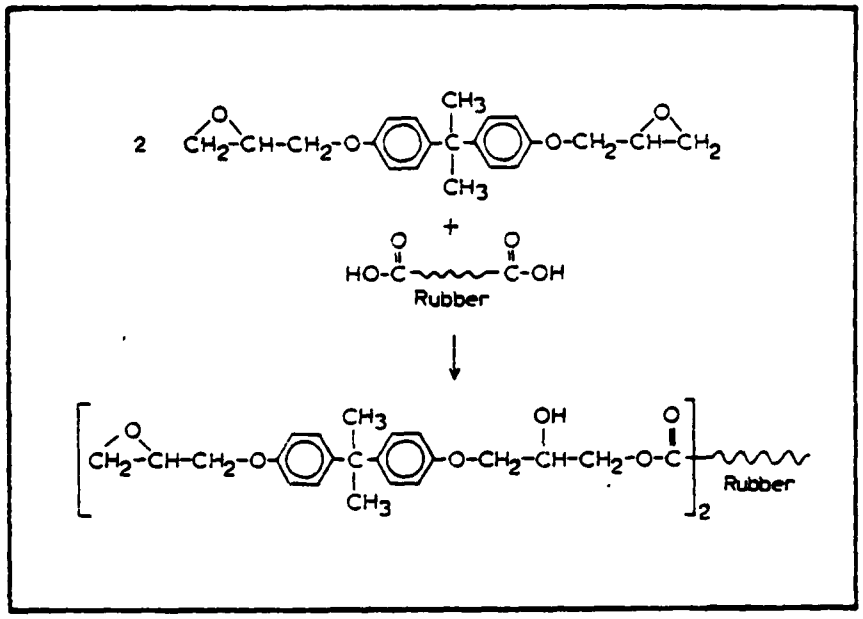
Scheme 1




particles. More recently, the use of butadiene-acrylonitrile rubbers terminated with amino groups has been investigated. These types of modifiers have been reviewed recently by Riew (10) and have also been discussed in detail by Drake et al. (11).

The butadiene acrylonitrile rubbers have clearly been successful to a considerable extent in improving the toughness characteristics of epoxy networks. However, since the butadiene component of the elastomer contains unsaturation, it would appear to be a site for premature thermal and/or oxidative instability. One would imagine that excessive crosslinking could take place with time which would detract from the otherwise desirable improvements accomplished with these structures.

We have been interested for some time in the chemistry and structure of polysiloxane containing systems. We suggest that some of the important characteristics of siloxane structures, such as their thermal and oxidative stability, low glass transition temperature, hydrophobic character and low surface energies could perhaps render them useful as epoxy modifiers. In order to do so, however, one would have to consider the questions of functionality, both with respect to type and concentration and also the miscibility or solubility of such hydrophobic nonpolar materials in the typically aromatic based epoxy precursors. Thus, the definition of such functional oligomers and their network forming characteristics appear to be a logical starting

place for these investigations. This paper will describe our initial studies which have been concerned both with the synthesis of appropriately functionalized siloxane oligomers, their chemical characterization and with the development of the siloxane modified networks. Future papers will discuss the property modifications and characteristics in more depth.

## EXPERIMENTAL

### 1. Synthesis of the Epoxy Terminated Disiloxane Precursor

The epoxy disiloxane was made in our laboratory by the hydrosilation reaction of allylglycidylether (Aldrich) with dimethylchlorosilane which was obtained from Petrarch. The reaction was conducted as a 50% solution in toluene, and was catalyzed by chloroplatinic acid at a concentration of approximately $10^{-3}$ moles per mole allylglycidylether. The reaction proceeded rapidly at 35°C as evidenced by a pronounced exotherm. Although it is felt that most of the reaction is completed very quickly, perhaps within five minutes or less, heating (35°C) was continued for approximately one hour. The molar ratio of the allylglycidylether to the dimethylchlorosilane was about 1.3 to 1. The excess allylglycidylether was utilized to insure that all of the Si-H bonds were in fact reacted. The product was purified by vacuum distillation at 1.0 torr and 90°C. The chlorine substituted silane was then hydrolyzed in water to produce the desired disiloxane. The resulting product was colorless, transparent and was fully characterized by proton NMR as being consistent with the desired structure. Moreover, the boiling point was shown to match the value given in the literature (12).

### 2. Preparation of the Siloxanolate Equilibration Catalyst

In order to induce the polymerization of the cyclic tetramer in the presence of these functional siloxanes, a siloxanolate catalyst was prepared from the reaction of 4 moles of the cyclic tetramer ($D_4$) with 1 mole of pure tetramethylammonium hydroxide. In one approach, the solid was dispersed in the liquid $D_4$ and the reaction was conducted under an argon stream for about 48 hours at 60-70°C. The rapid argon flow was sufficient to dehydrate the system. The reaction when conducted under these conditions is somewhat complex. After about 5 hours we have observed that the system appears rather opaque and that the viscosity is increased significantly. As a function of time, the viscosity begins to decrease and the material, while not becoming perfectly transparent, does increase in translucency relative to the original opaque mixture. The catalyst produced in this manner is sufficiently active for the synthesis of all the oligomers discussed in this paper. However, for other oligomers, such as silylamines, additional refinements appear to be necessary and will be

discussed in detail in future papers. Briefly, utilization of an azeotroping solvent such as hexane is desirable. Higher D-4/base ratios may also be used.

3. Equilibration Polymerization of Epoxy Functional Disiloxanes

The epoxy terminated siloxanes were produced via the so-called equilibration polymerization of the previously mentioned disiloxane discussed in Section 1 above through the use of the quaternary ammonium siloxanolate catalyst discussed in Section 2. The molecular weights of the siloxanes were varied via controlled ratios of the cyclic tetramer ($D_4$) to the epoxy disiloxane "end-blocker". The reactions were conducted at 80°C for various periods of time that ranged to as much as 44 hours. The catalyst concentration of the siloxanolate discussed in 2 above was varied from approximately 0.1% to as high as 1% by weight based on the total concentration of reactants. The reaction was followed by both GPC and also titration methods which are described more fully in a later section of the experimental. After the appropriate reaction time, the temperature was increased to about 150°C for approximately another 3 hours. This time is believed sufficient to decompose the so-called transient catalyst (13) and thus inactivate the equilibration process. At this point, the oligomer also contains cyclics. In order to remove the cyclics, the crude oligomers were vacuum stripped under mechanical pump vacuum at approximately 0.5 to 1 torr and about 100°C. The stripped materials are then characterized further as discussed below. Typically, the stripped materials are perfectly transparent. An alternate method for purification of the crude oligomers is to extract the equilibrium cyclics with a solvent such as methanol which will dissolve the cyclic but will not dissolve oligomers of ~1000 molecular weight or higher.

4. Equilibration of Aminopropyl Terminated Disiloxanes

The aminopropyl terminated disiloxane was obtained from Petrarch, although one could in principle prepare this as discussed earlier by hydrosilation procedures. The equilibrations were conducted by reacting the cyclic tetramer in the presence of bis(aminopropyl)tetramethyldisiloxane and about 0.5 weight percent of the siloxanolate catalyst at 80° for 44 hours. These conditions were selected on the basis of earlier extensive studies with the epoxy terminated oligomer. Again, the catalyst was decomposed by reaction at 150°C for 3 hours prior to the extraction of the cyclics. The resulting amino terminated oligomer molecular weight is governed largely by the ratio of the cyclic tetramer to the disiloxane. It was worked up in an analogous manner to the epoxy systems, e.g. either by vacuum stripping or by treatment with methanol.

## 5. Equilibration of Carboxypropyl Terminated Siloxanes

The carboxypropyl functional disiloxane was obtained from Silar Laboratories, Scotia, New York. Unlike the previous two equilibration systems, it was necessary here to utilize an acid catalyst. We investigated several systems, but here we described how we have utilized trifluoroacetic acid. The carboxy terminated disiloxane and the $D_4$ were mixed in appropriate ratios and the temperature was brought to 60°C. At this point about 14% of pure trifluoroacetic acid was introduced. The reaction was allowed to proceed for 24 hours and one could observe the viscosity increasing slowly as a function of time. Other time intervals were investigated and 24 hours appeared to be approximately the optimum period for this particular synthesis. The reaction was also followed by a GPC method as discussed below. In this case, the product was purified by repeated washing of the crude oligomer with distilled water in order to remove the excess acid catalyst. The washings were continued until one could no longer observe any fluorine present, especially as judged by $^{19}F$ NMR experiments. After the oligomer has been sufficiently washed with distilled water, it was extracted from the aqueous suspension via diethyl ether. The diethyl ether was removed by a rotary vacuum stripping apparatus. The residual cyclic oligomers were devolatilized as indicated for the systems above, that is at about 0.5 torr and approximately 100°C.

## 6. Synthesis of Piperazine Terminated Disiloxanes from the Reaction of Carboxy Functional Disiloxane and Aminoethyl Piperazine (AEP)

The carboxy terminated disiloxane discussed above was mixed with an excess aminoethyl piperazine (Aldrich) and subsequently heated to 160°C for 24 hours. The reaction was followed by studying the FTIR spectrum which indicated the formation of the amide bond as a function of time and the disappearance of the carboxyl group. In addition, the material was characterized via titration methods. The titrations included both those for the carboxyl group and the secondary piperazine endgroups. Before the titrations were conducted, the excess amine was stripped from the crude reaction material under high vacuum. The titration of the stripped reaction product indicated the expected molecular weight. This was further confirmed by molecular weight measurements by vapor pressure osmometry in chloroform solvent at 37°C. Both the FTIR spectra (10) and the absence of a second endpoint in the potentiometric titrations indicate that only the secondary piperazine amine endgroup is present.

7. Equilibration of Piperazine Capped Disiloxanes

The piperazine capped disiloxane as discussed in 6 above could easily be equilibrated under exactly identical conditions to those discussed for the primary amine system earlier, that is, the disiloxane, cyclic tetramer, and 0.5 weight percent of the siloxanolate catalyst were heated to 80°C for 44 hours. The work-up procedure was identical, that is, the catalyst was deactivated at 150°C for 3 hours. The excess cyclics were then stripped under vacuum (0.5 torr, 100°C) and the material was further characterized by amine endgroup titration.

8. Piperazine Capping of Epoxy Terminated Siloxane Oligomers

An additional way to produce a secondary amine group utilized the reaction of 8 moles of piperazine with 1 mole of the epoxy terminated siloxane oligomer. This reaction was conducted in dioxane at 60° for about 24 hours. Excess piperazine was removed by washing the oligomer extensively with distilled water. Since the piperazine is water soluble and the oligomer is not, the final system was easily purified to very low levels of residual piperazine in this manner. The product was characterized by titration of the amine endgroups.

9. Synthesis of the Modified Epoxy Networks

For the purposes of this study, we have utilized commercially available epoxy oligomers based on bisphenol-A and epichlorohydrin. These particular oligomers were kindly supplied by the Shell Development Company (EPON resin-828). The basic route to thermoset formation that we have utilized has been to react stoichiometric quantities of diamines with the epoxy network precursors. The amine that we have primarily worked with is bis(para-aminocyclohexyl)methane which was generously supplied by the DuPont Company under the trade name PACM-20. Test specimens were usually prepared in silicone molds which were purchased from Dow Corning under the trade designation of #3110 Silicone Rubber. The conditions for network formation were investigated for the control systems and it was decided to utilize two different conditions, a so-called one-step and a two-step process. In the one-step process, the two components were first degassed separately in a vacuum oven at about 30 torr and 50°C. Once they were sufficiently degassed they were quickly mixed to form a homogeneous solution and cast into the silicone molds at 160°C. The reaction was allowed to continue under these conditions for two hours, which appears to be sufficient time to basically complete the reaction. It is also above the glass temperature of the final network structure. In the two-step process, the epoxy (EPON resin-828) and the modifier were first mixed at 60°C for about 2 hours. Subsequently, the degassed PACM-20 was added and

the mixture was then poured into the silicone mold at 160°C for 2 hours as was done for the one-step process. Note that the two-step process has been exclusively utilized for the piperazine capped epoxy siloxane modifiers. In both processes, the materials were removed from the mold after the 2 hour curing cycle and cooled down to room temperature. The networks prepared in the manner described above were utilized for thermal and mechanical studies but not for ESCA spectroscopic studies. Those samples were prepared differently as discussed below.

## 10. Characterization

### a. Titrations

The functional epoxy oligomers and their precursors were characterized by a number of methods. The titration method utilized a Fisher Model II® automatic titrator which was capable of derivative measurements and utilized basically a potentiometric titration mode. The epoxy groups were titrated according to standard procedures discussed in the literature (14). Carboxy and amine groups were simply titrated with either base or acid which enabled one to observe appropriate potentiometric endpoints. Indicators were also utilized to complement the potentiometric studies. In the case of the epoxy oligomers, we used crystal violet; for the amine oligomers, bromophenol blue was employed. The titrations of the epoxy group via the potentiometric method did require a carefully purified solvent. We utilized chlorobenzene as a solvent which had been previously treated with concentrated sulfuric acid to remove any olefinic structures, followed by washing with water and careful fractional distillation.

### b. NMR

Proton NMR was used routinely to confirm a number of the structures, especially those of the disiloxanes. In general, these measurements utilized a Varian EM-390 at room temperature with a methylene chloride or benzene chemical shift reference. The measurements were conducted in deuterated chloroform.

### c. Gel Permeation Chromatography (GPC)

A Water's instrument model 440 was utilized at room temperature. The columns were microstyrogel of the following sizes (500Å, $10^3$Å, $10^4$Å, $10^5$Å). Toluene solvent was used together with a differential refractive index (DRI) detector. The concentration of the oligomers in toluene was about 0.5 weight percent and the flow rate was approximately 1 ml/minute. The procedure described above appeared to be successful for the epoxy

terminated oligomers and the carboxy terminated oligomers. Unfortunately, the aminopropyl and piperazine terminated oligomers showed anomalous behavior which we believe is a function of the absorption of the amine groups onto the packing materials. Therefore, our discussions will be limited to the epoxy and carboxy capped materials. The GPC did clearly distinguish between the disappearance of the cyclic tetramer and the formation of the oligomeric species during the course of the equilibration reactions discussed above.

d. Differential Scanning Calorimetry (DSC)

Thermal analysis measurements via DSC were utilized both to follow the curing reaction and to characterize the precursor and network materials. The general techniques for following reactions by differential scanning calorimetry are well established and can be reviewed in reference 15. We have also discussed the procedures for this type of an experiment in one of our earlier publications (16). A Perkin-Elmer Model 2 instrument was utilized.

e. X-Ray Photoelectron Spectroscopy (XPS, ESCA)

Surface analysis measurements were conducted on the siloxane modified epoxies using a DuPont 650 ESCA instrument in the MCA mode (Mg anode operating at approximately 22 milliamperes and 10kV). The samples for ESCA were prepared somewhat differently than those previously mentioned. In this case, the systems were mixed and cast directly onto the ESCA probe. This was done in an attempt to avoid the contamination of the surface with siloxane moieties that might be present in the silicone molds. Note that extreme care must be utilized in preparing such samples to avoid the somewhat ubiquitous contamination of siloxanes in the system. In fact, it was necessary to utilize a different laboratory to prepare the mixtures for these experiments. In this case, one could prepare control surfaces that were apparently free of extraneous siloxane contamination. The control samples were utilized together with various levels of siloxane modified systems, especially those derived from the piperazine capped epoxy oligomers. In addition, networks prepared with the epoxy oligomers themselves and the aminopropyl terminated oligomers were investigated via this surface technique.

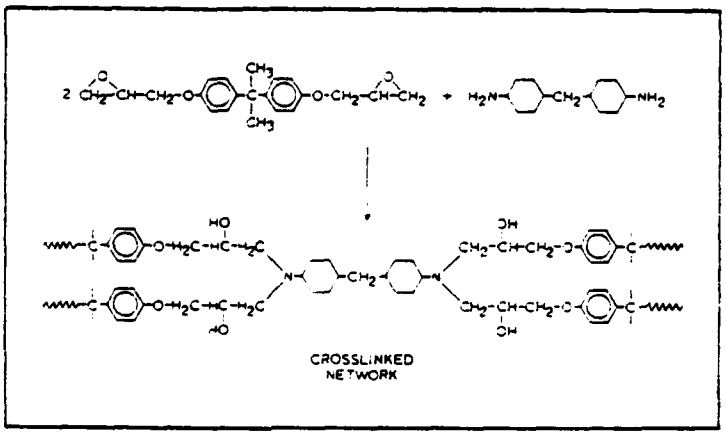
f. ATR-FTIR Investigations

We have briefly investigated the cured and modified specimen via ATR-FTIR spectroscopy. A Nicolet MX-1 FTIR with a 45° KRS-5 crystal at an incidence angle of 50° was used. The FTIR spectra were obtained on several samples and were complementary to the ESCA in estimat ng the surface behavior of these modified systems.

## RESULTS AND DISCUSSION

An idealized reaction of a diglycidyl ether of bisphenol A with a diamine is depicted in Scheme 2. Ideally one should

Scheme 2



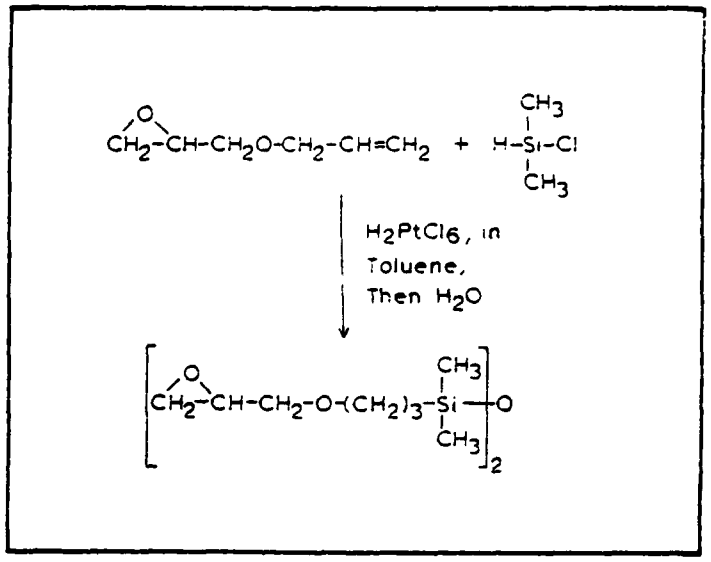

generate four function points from each diamine molecule and therefore one could imagine a relatively uniform network density in such systems. While the question of network density is of great interest, it is not of primary concern to this paper, even though there may well be fewer than four functions per crosslink and conceivably the crosslinks may be somewhat non-uniform. We will discuss this point further in future papers that attempt to relate morphology to physical behavior. Our control systems were prepared from the EPON resin-828 and the cited bis(p-aminocyclohexyl)methane.

### Synthesis of Functional Polydimethylsiloxane Oligomers

The oligomers utilized in this study to date have been prepared by the equilibration polymerization of a cyclic tetramer in the presence of functional disiloxanes utilizing a

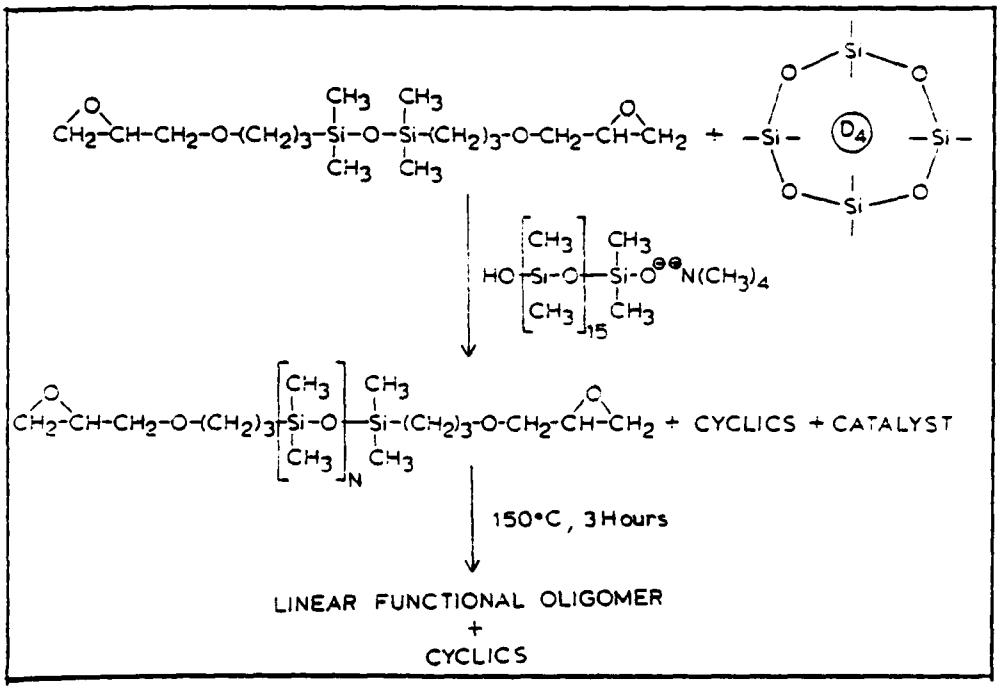
siloxanolate catalyst. The disiloxanes themselves were either synthesized in our laboratory or purchased. For example, in Scheme 3 we show one route that was utilized to prepare a diepoxy disiloxane endblocker. The reaction proceeds very rapidly at 35° as discussed in the experimental section. The reaction product can be further purified by vacuum distillation

Scheme 3




at approximately 2 torr and 185°C. The product obtained displayed the correct proton NMR spectrum and is a relatively non-viscous clear liquid. The actual equilibration then to produce the epoxy terminated siloxanes is illustrated in Scheme 4. Here one introduces the disiloxane, the cyclic tetramer, and a catalytic quantity of the siloxanolate catalyst. The reaction temperature is 80°C for a period of time up to 44 hours. The reaction proceeds by attack of the siloxanolate on the silicon atom of the cyclic monomer to open the ring (initiation). The propagation step consists of further anionic attack on the cyclic monomers. As a function of time, the growing siloxanolate chain ends are able to attack the silicon oxygen bond in the disiloxane, thus becoming incorporated between the two epoxy endgroups. Since the silicon carbon bond in the disiloxane is not cleaved under these conditions, eventually at equilibrium the cyclic tetramer is incorporated to approximately 85% or higher into the chain which is capped perfectly with epoxy functionality. The residual $D_4$ is converted into cyclics which may be removed after catalyst deactivation by vacuum stripping as discussed in the experimental section. Alternatively, one may

Scheme 4




wash out the cyclic oligomers with methanol. Note that higher alcohols may not be used since they will also dissolve the oligomer. Prior to extraction of the cyclics, the catalyst is deactivated by heating to about 150°C for 3 hours. The catalyst undergoes a Hoffman-like degradation to yield inert products, and hence it is termed a "transient catalyst" (13). It was very interesting and perhaps surprising to note that the epoxy terminated disiloxane could be effectively equilibrated with a basic siloxanolate-like catalyst. We were naturally concerned that the siloxanolate catalyst might also attack the epoxy groups on the disiloxane. Fortunately, this does not seem to be the case if one chooses the reaction conditions appropriately. For example, in Table I, we list some endgroup analyses that were conducted following the redistribution of the diepoxy system. We utilized, as discussed in the experimental section of this paper, a standard titration for the endgroups and compared the theoretical value on the basis of the ratio of the cyclic tetramer to the disiloxane to the actual equivalent weight which was measured by the titrations. This was also studied as a function of concentration of the siloxanolate catalyst ranging from about 0.1 to 1.0 weight percent. Various times up to 44 hours were investivated. As one may note, in most cases it appears that the equivalent weight is in good agreement with the theoretically predicted equivalent weight and any deviations are within experimental error. A control experiment was also

Table I

COMPARISON OF THEORETICAL AND EXPERIMENTAL EPOXY GROUP CONCENTRATIONS IN SILANOLATE EQUILIBRATED EPOXY FUNCTIONAL POLYDIMETHYLSILOXANE OLIGOMERS

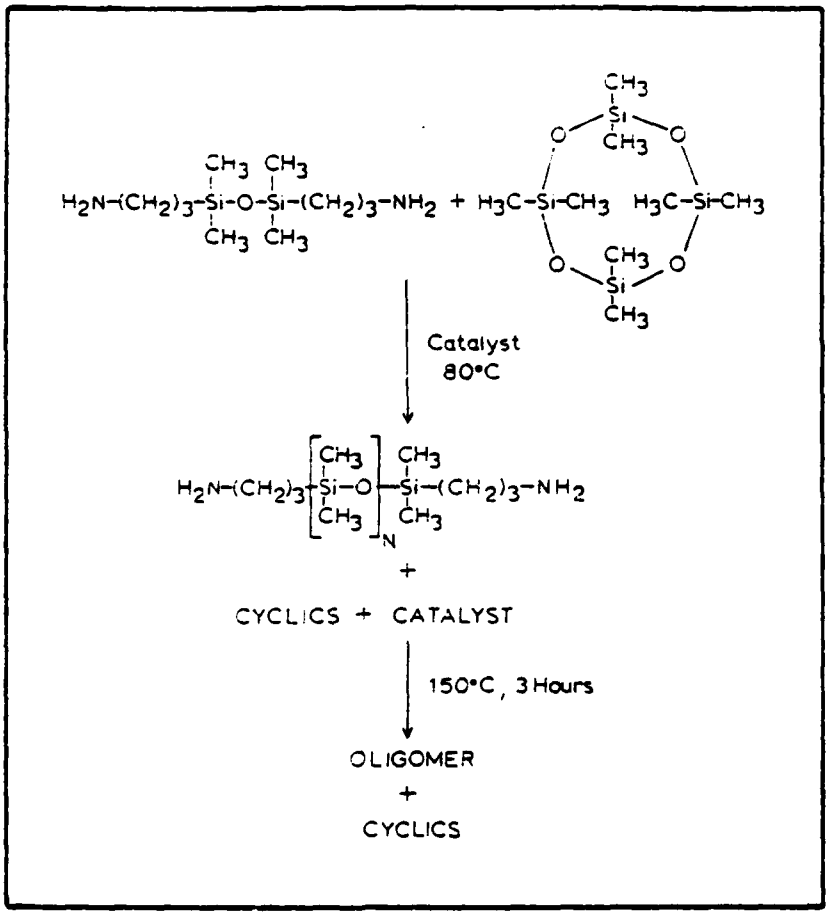
| $\langle M_N \rangle$ (THEORY) | EPOXY EQUIV. WT. (THEORY) | TITRATED EQUIV. WT. | WT. PERCENT EQUILIBRATION CATALYST | EQUILIBRATION TIME, (HOURS) AT 80°C |
|---|---|---|---|---|
| 360, Dimer | 180 | 190 | -- | -- |
| Control | 180 | 180 | 0.5% | 22 |
| 5000 | 2500 | 2250 | 0.5% | 22 |
| | 2500 | 2525 | 1.0% | 22 |
| 5000 | 2500 | 2350 | 0.5% | 44 |
| | 2500 | 2750 | 1.0% | 44 |

conducted which used only the siloxane dimer and the silanolate catalyst (Table I, Control). After 22 hours at 80°C, there was no evidence that the epoxy group had been attacked by the silanolate. Therefore, on the basis of this result and some other data to be discussed later, we feel that the siloxanolate catalyst must be too weak a base to significantly attack the epoxide oxirane ring, especially when the reaction is conducted in the presence of the readily available siloxane bond. It is well known, for example, that alkoxides are much stronger bases than siloxanolates or silanolates and this seems to be a key point in this functional oligomer synthesis. We were also concerned with how one could follow equilibrations of this type. We chose to utilize gel permeation chromatography (GPC) data as a function of catalyst concentration as shown in Figure 1. We have shown here the elution time as a function of catalyst concentration after 44 hours of reaction time at 80°C. It appears that under the conditions we have utilized, 0.1% of the "bulk" prepared catalyst (e.g. no azeotroping solvent) is sufficiently active to initiate the equilibration. However, at 0.5% catalyst one sees clearly the disappearance of the cyclic tetramer and the formation of a most probable unimodal molecular weight distribution for the oligomer. Higher catalyst levels appears to produce somewhat higher rates. Complementary data of the effect of time on the epoxy terminated polydimethylsiloxane redistributions is shown in Figure 2. Again, one notes that certainly after 44 hours, the apparent equilibrium concentration of oligomers is reached.

The transient equilibration catalyst preparation is important. In order to synthesize the catalyst, one may react a quaternary ammonium hydroxide with the cyclic tetramer. An important variable to consider is the ratio of the cyclic tetramer to the quaternary ammonium salt. For this work, we have utilized a molar ratio of 4:1, that is, 4 moles of $D_4$ per mole of quaternary ammonium hydroxide. With the conditions utilized here, one presumes to have an average siloxane degree of polymerization of about 15 with a siloxanolate type end group. Alternatively, the silanol groups may couple and the siloxanolate may in fact be difunctional. The active catalyst chain end can be determined by a standard titration with for example, alcoholic HCl. It is important, of course, to dehydrate the system quite effectively for the purposes of this research. As discussed in the experimental section, we utilized initially merely a rather strong argon flow to achieve this dehydration. Other methods may also be used. For example, one may efficiently azeotrope the water with hexane or benzene. Note also that to equilibrate the disiloxanes discussed in this paper, even the catalysts dehydrated with argon work quite well. With more sensitive systems, such as silylamine functionalities, it is necessary to effectively dehydrate and to utilize a higher ratio of the cyclic tetramer to the base.

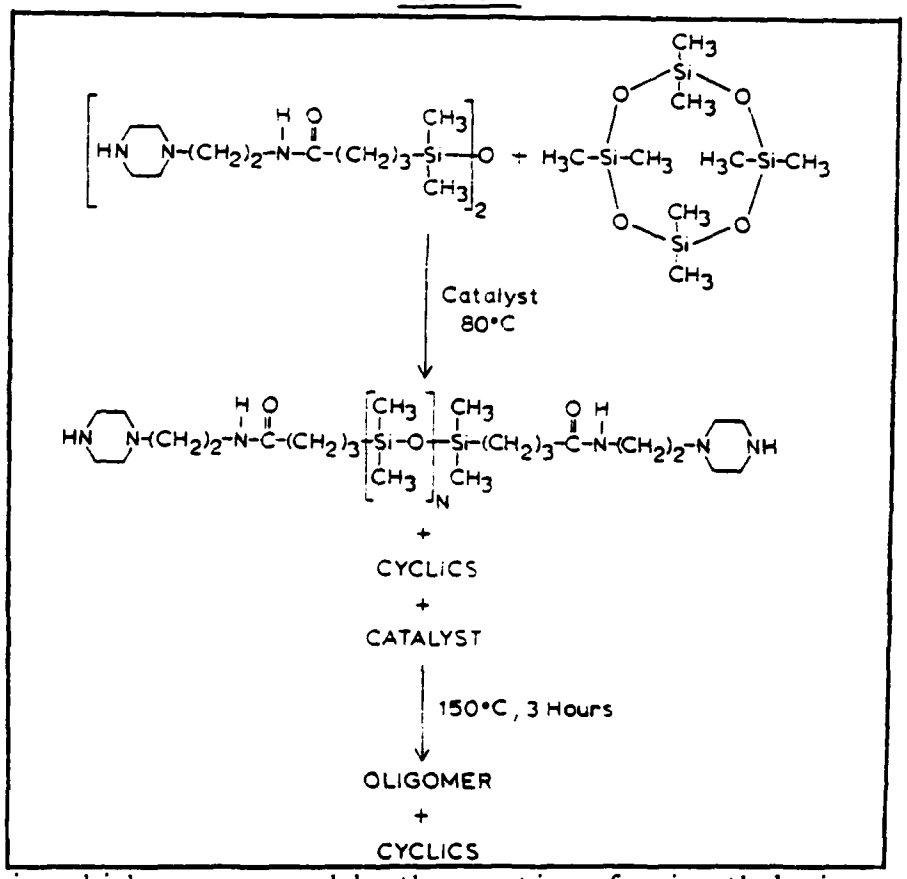
The equilibration of the aminopropyl terminated disiloxane was conducted in a very similar manner to the epoxy terminated disiloxane and is shown in Scheme 5. The reaction in this case could not be followed by our GPC unit since we noticed significant absorption of the oligomers onto the columns. Perhaps other columns would be more suitable and this question is being further explored. One approach that seems to be successful is to cap the end groups with trifluoroacetic anhydride, or benzoyl chloride.

Scheme 5



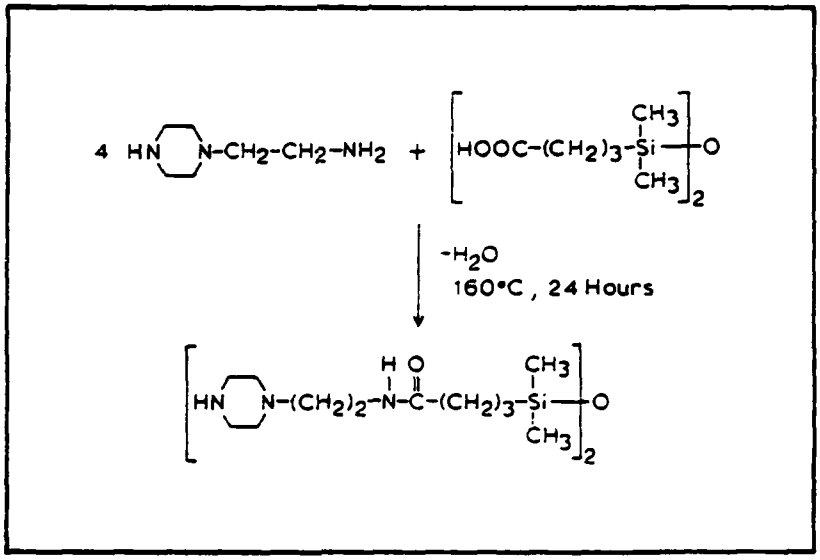
A very similar equilibration was conducted as shown in Scheme 6 for the synthesis of secondary amine terminated siloxane oligomers. The amine terminated disiloxane here is a secondary

Scheme 6

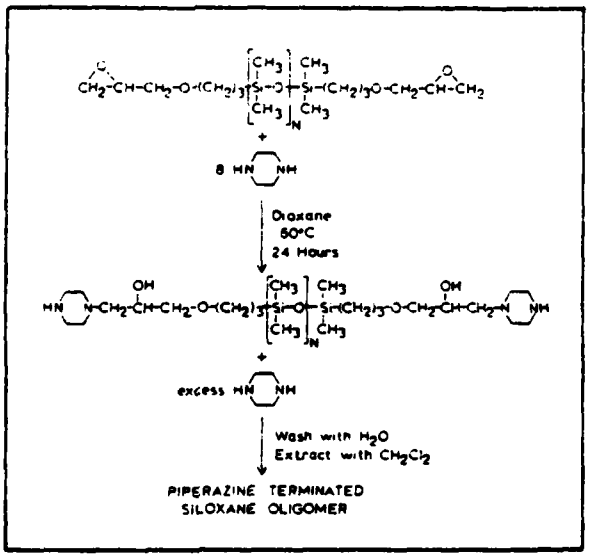



amine which was prepared by the reaction of aminoethyl piperazine (AEP) with a biscarboxypropyldisiloxane. The carboxypropyldisiloxane was obtained from Silar Laboratories and presumably could be synthesized by hydrolysis of a nitrile derivative. We prepared the piperazine capped disiloxane by a bulk reaction at 160°C for 24 hours. The reaction product was purified by vacuum stripping of the aminoethyl piperazine. The resulting residual product gave only amine like titrations and a clearly defined amide band could be observed in the infrared. In addition, the infrared spectrum showed a negligible if any concentration of residual carboxyl groups. The synthesis and structure for the disiloxane is shown in Scheme 7. A different type of secondary amine functionality was prepared by capping of the epoxy terminated oligomer with an excess of piperazine as shown in Scheme 8. In this case, the epoxy oligomer was dissolved in dioxane and 8 moles of piperazine were added. The

Scheme 7




Scheme 8

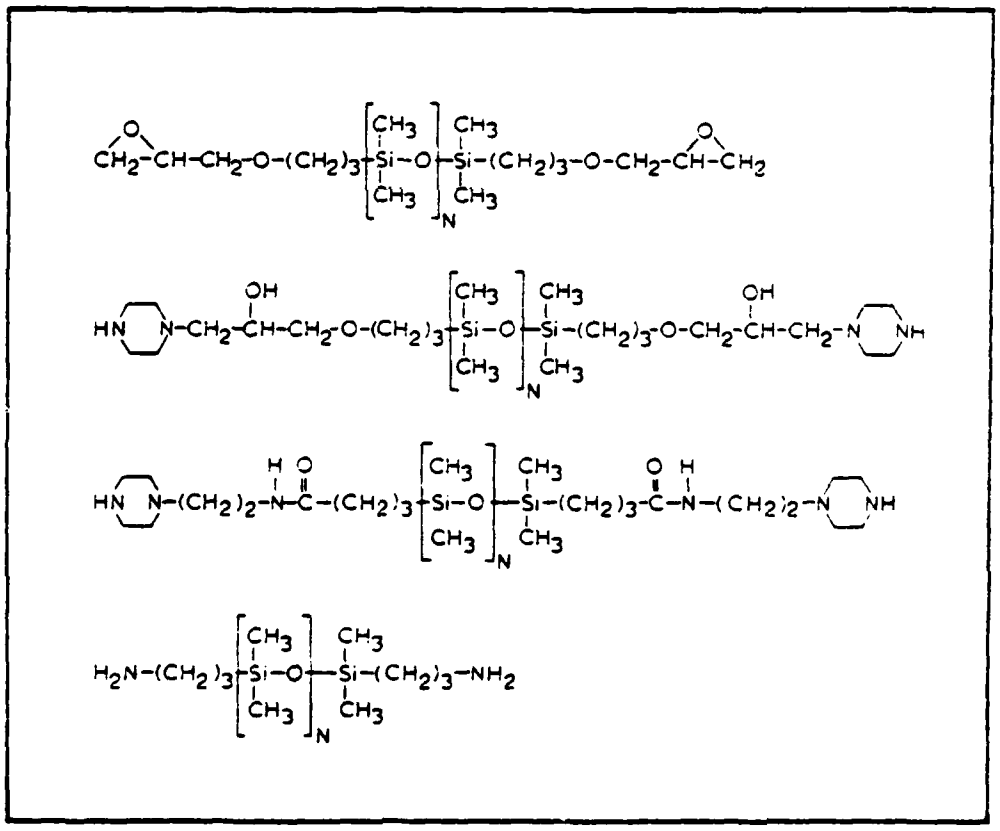


material formed a homogeneous solution at 60°C and was allowed to react at that temperature for 24 hours. At this time, the reaction product was cooled down and thoroughly washed with distilled water. The water served to remove the excess piperazine. Next, the residual product was extracted with methylene chloride and vacuum stripped. The resulting derivative does in fact have a piperazine endgroup. However, unlike the previously discussed secondary amine this product also contains a hydroxyl group resulting from the cleavage of the epoxy group.

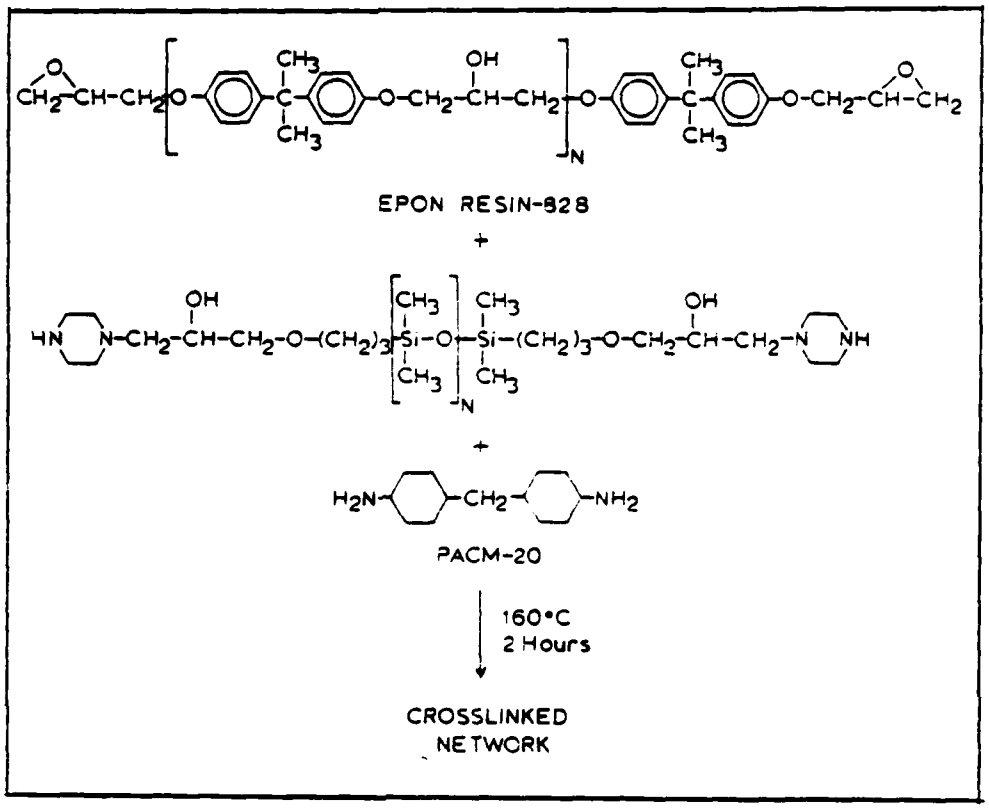
## Network Formation Studies

The general structures of the siloxane modifiers that we have utilized in this study are shown for comparative purposes in Scheme 9. The overall curing reaction is depicted in Scheme 10. In this case we have illustrated the reaction by using the

Scheme 9



Scheme 10




piperazine capped diepoxy systems. Reactions were, in general, conducted for two hours at 160°C to produce a stable, well crosslinked network. The concentration of the modifiers was varied. The curing reaction was studied with the various siloxane modifiers already mentioned in Scheme 9. However, here it is important to note the question of miscibility. In order for the modifier to be effective, one imagines that it must first be reasonably miscible with the epoxy oligomer and subsequently perhaps microphase separate as small domains during the progress of the curing reaction itself. In the work described in the literature (10) utilizing butadiene/acrylonitrile reactive liquid polymer, one presumably incorporates acrylonitrile into the system to obtain an appropriate solubility parameter such that the liquid rubber will be miscible with the epoxy precursor, such as EPON Resin-828. In the case of siloxanes, the situation is somewhat more difficult. Pure polydimethylsiloxane has a calculated solubility parameter of about 7.6, which is much lower than that of the epoxy oligomers. Thus, when we tried to mix the epoxy terminated siloxanes with the EPON resin-828, it was quickly observed that the systems were highly incompatible (immiscible). If one attempts to prepare a cured specimen from

the epoxy capped siloxanes of this type, one finds that the resulting product is extremely heterogeneous in a non-controllable way and that indeed unreacted liquid siloxane remains in the otherwise cured specimen after the time cycle mentioned. The aminopropyl siloxane oligomers appeared to be somewhat better but yet they were not highly miscible either. Additional problems with inhomogeneities were observed in this system. Moreover, in this case, the primary amine group on the siloxane modifier is capable itself of prematurely gelling the epoxy system. In order to circumvent these problems, it occurred to us that secondary amine systems might be of considerable interest. These modifiers can be prereacted with the EPON resin-828 since they should only react under moderate conditions with one epoxy group, it should be possible to prepare linear soluble precursor. Indeed, the reaction shown in Scheme 10 utilizing the piperazine capped epoxy oligomers was much different than all that had been studied prior to that point. The materials in this case apparently react to form homogeneous mixtures of the siloxane modifier and the EPON resin-828. In general, this reaction of the modifier with the EPON resin-828 was allowed to proceed for 2 hours at 60°C prior to introduction of the curing agent (PACM-20). The curing agent was added with rapid stirring. The mixtures of the active components were then cast into a silicone mold as described in the experimental. The curing step was conducted for 2 hours at 160°C. This temperature was chosen since we were able to demonstrate, as will be discussed later, that the glass transition temperatures were no higher than 150°C. Therefore, one would expect the reaction temperature would be sufficient to provide adequate mobility for the chain ends to react and generate the network structure. The other modifiers were reacted similarly to those in the above described procedure. In order to follow the reaction during the curing stage, we utilized differential scanning calorimetry. A variety of disiloxanes noted as "DSX" and polysiloxanes noted as "PSX" were utilized. In Figure 3 we show a comparison of the conversion temperature behavior for dynamic DSC scans utilizing a heating rate of 10°C/minute. Sample 3 in Figure 3 may be considered to be the control experiment utilizing the cycloaliphatic diamine as the curing agent. Sample 4 illustrates the reaction of the epoxy disiloxane with the standard curing agent, again PACM-20. One may note from this curve that the fastest reaction is obtained with the piperazine capped disiloxane system. All of these reactions were conducted in this case at 1:1 stoichiometry. The aminopropyl disiloxane also reacts quite fast although not as fast as the piperazine adduct. It is important to note that by far the slowest reaction was observed between the epoxy disiloxane and the PACM-20 curing agent. Additional information concerning the reaction rate of these various materials is provided in Figure 4. Here again the same designations that were noted in Figure 3 are applicable.

One observes again that, as a function of time, by far and away the fastest reaction is observed with the piperazine capped disiloxane. Indeed, even at 80°C, it is very rapid and was too fast to follow by DSC at 100°C. The piperazine capped siloxane oligomer reacts very rapidly at 100°C, even faster than the aminopropyldisiloxane at 100°C. The curing agent control, as shown in the dark triangles, is much slower at 100°C than the modifiers discussed above. Hence, the modifiers should be reacted or used up faster than the curing agent in the ultimate systems of interest. Again, as was shown in Figure 3, by far the slowest reaction of this series studied was the epoxy disiloxane reacted with the PACM-20 curing agent. Its reaction, even at 140°C, was very slow. This no doubt at least partially explains why attempts to incorporate the epoxy capped siloxane into the network were unsuccessful. That is, the reaction rate was so slow that most of the epoxy terminated oligomers were not incorporated, and hence, simply remained as incompatible additives after the curing reaction. The additional data derived from the DSC studies are shown in Table II. The reaction enthalpies were derived and appear to be in a reasonable region for this type of reaction.

Representative glass temperatures for a control and for modified systems prepared during this study are shown in Table III. In general, the glass temperatures of the PACM-20/EPON resin-828 system appear to be approximately 150°C. The effect of the modifier on the glass temperature of the network is very markedly dependent upon the length of the siloxane system. This point will be further addressed in future papers. Disiloxanes can in some cases plasticize the network whereas longer chains appear to develop a second microphase and therefore have only a nominal depression of the principal glass transition temperature.

## Surface Analysis of Siloxane Modified Networks

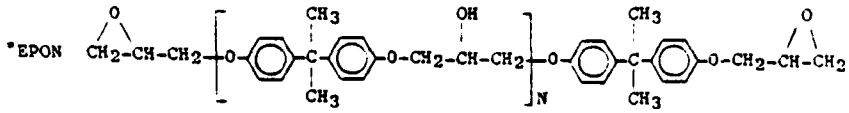
### a) ESCA

Electron spectroscopy has been utilized by a number of investigators to study the surface behavior of block copolymers and block copolymer/homopolymer mixtures (17-19,24,25). Generally the ESCA experiment is expected to allow one to ascertain the surface structure of perhaps the top 40 or 50 Å near the surface (20,21). We have thus far investigated the possible surface segregation of the cured epoxy systems by ESCA using three different modifiers, the epoxy dimer, the aminopropyl dimer and the hydroxypiperazine dimer. In addition, we also utilized oligomers based on the epoxy systems and also the hydroxypiperazine capped system. The data we have obtained is summarized in Table IV. Four low levels of siloxane were investigated ranging from 0.1% up to 2% by weight. Let us focus our attention first on the three dimers. By assessing the ratio

## Table II

HEATS OF REACTION FOR THE CURING OF EPOXY-AMINE SYSTEMS AS OBTAINED BY DSC

| SYSTEM | $\Delta H_{Rxn}$ (kCal/eq) |
|---|---|
| EPON 828* + $H_2N$-⟨⟩-$CH_2$-⟨⟩-$NH_2$ | 22.8 ± 1.3 |
| EPON 828* + $H_2N$-DSX-$NH_2$ | 25.4 ± 1.2 |
| EPON 828* + HN⟨⟩N-PSX-N⟨⟩NH (a) | 19.3 ± 1.5 |
| EPON 828* + HN⟨⟩N-DSX-N⟨⟩NH (b) | 24.4 ± 1.1 |
| ▽DSX▽ (O, O) + $H_2N$-⟨⟩-$CH_2$-⟨⟩-$NH_2$ | 23.8 |




(a) Piperazine Capped Epoxy Functional Oligomeric Polydimethylsiloxane ($M_n$ = 4,200)

(b) Piperazine Capped Epoxy Disiloxane

Table III

GLASS TRANSITION TEMPERATURES OF SILOXANE MODIFIED EPOXY NETWORKS [a]

| Sample # | Siloxane Modifier Type | MW | % Wt | Tg (°C) |
|---|---|---|---|---|
| 1 | Aminopropyl | 248.5[b] | 4.0 | 127 |
| 2 | Aminopropyl | 248.5 | 10.0 | 113 |
| 3 | Aminopropyl | 2000 | 6.5 | 148 |
| 4 | AEP[c] | 850 | 10.0 | 146 |
| 5 | AEP | 2750 | 10.0 | 150 |
| 6 | PIP.[d] | 4200 | 8.0 | 147 |
| 7 | PIP. | 4200 | 10.0 | 149 |
| 8 | CONTROL (EPON Resin-828 + PACM-20) | | | 150 |

(a) DSC, 10°K/Minute

(b) Dimer

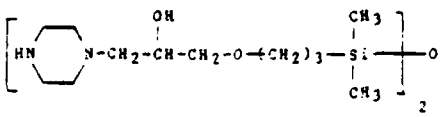
(c) Aminoethylpiperazine capped PSX

(d) Piperazine capped PSX

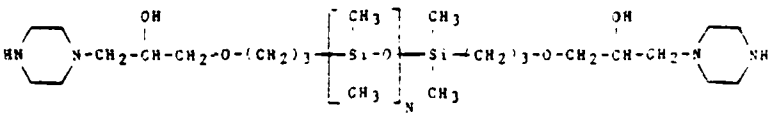
## Table IV

**ESCA C/Si RATIOS OF VARIOUS FUNCTIONAL DIMER AND OLIGOMERIC POLYDIMETHYLSILOXANE MODIFIED EPOXY NETWORKS** (a)

| WT. % SILOXANE | EPOXY DIMER | AMINOPROPYL DIMER | PIPERAZINE* DIMER | EPOXY** OLIGOMER | PIPERAZINE*** OLIGOMER |
|---|---|---|---|---|---|
| 0.1 | 17.3 | -- | 200 | 2.3 | 3.4 |
| 0.5 | 9.7 | 15.9 | 179 | 2.1 | 3.9 |
| 1.0 | 6.1 | 16.4 | 161 | 1.9 | 3.3 |
| 2.0 | 9.1 | 9.0 | 125 | 1.9 | 2.9 |

* 

** 2900 g/mole

*** 4200 g/mole 

(a) A C/Si ratio of 2.0 would be indicative of a siloxane-like surface

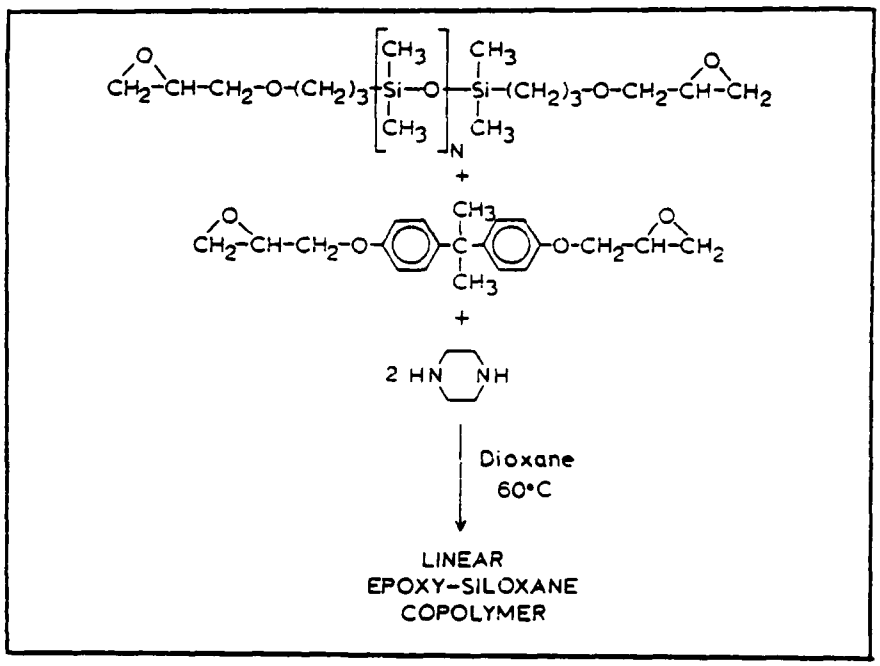
of carbon to silicon as judged in this manner, if one had pure siloxane on the surface, the carbon to silicon ratio should be exactly 2.0. Clearly, in all of the dimers this is not the case, which indicates that for the dimeric modifiers significant amounts of epoxy resin-828 units are near the surface. However, it is appropriate to point out that the piperazine dimer is quite different from either the epoxy dimer or the aminopropyl dimer. The high ratios here imply that in fact very little of the siloxane dimer is on the surface in the case of the piperazine dimer. This is reasonable since the simple disiloxane is in fact rather polar. On the other hand, the highest concentration of siloxane is observed with the epoxy disiloxane. This can be interpreted as being due to the fact that the epoxy system is the most incompatible of the three units compared here. The two oligomers studied included the highly incompatible epoxy oligomer which was basically not miscible at all with the EPON resin-828. Here one observes rather close to 100% coverage of the surface with siloxane (100% coverage would be a value of 2.0). In the case of the piperazine capped oligomer of about 4,000 molecular weight, it is clear that the surface is rather siloxane rich as judged by the relatively low C/Si values. However, under these conditions, it is not quantitatively covered by the siloxane. Nevertheless, one may observe significant physical differences in these systems as compared to the unmodified epoxy materials. They are indeed low energy surfaces even at this ratio. Additional work on this question of surface segregation using ESCA is being continued.

Some additional studies of the surface enrichment phenomenon were invesigated by using an ATR-FTIR study. In this case, we utilized siloxane modified epoxies, prepared by reacting the piperazine capped epoxy dimer or oligomer with EPON resin-828 and PACM-20. The infrared spectra of a network incorporating 2% of a piperazine oligomer as shown in Figure 5 may be contrasted with an analogous network with 2% piperazine capped siloxane dimer (Figure 6). The peak due to the siloxane at about 1011 or 1012 $cm^{-1}$ is much stronger in the piperazine oligomer than it is in the piperazine disiloxane system. This information is in agreement then with the ESCA data that showed the dimer to be much less capable of enriching the surface than the oligomer. Additional studies on the ATR modified systems are in progress for other oligomers in this series as well. It it clear however that both surface probes are in agreement. Also, the qualitative observations of the surface "feel" indicate that one has a great deal of enrichment of a siloxane on the surface relative to the concentrations that are present in the bulk. Additional quantitative work is being pursued with higher resolution instruments.

## Synthesis of Linear Copolymers

It is of interest to investigate whether linear soluble copolymers could be prepared from these systems. To do this, we utilized a reaction sequence shown in Scheme 11. The reaction was conducted by dissolving the epoxy capped siloxane oligomer and the bisphenol-A diglycidyl ether in dioxane to form about a 50% solution. The reaction was heated to 60°C and a stoichiometric quantity of piperazine was added. The reaction was allowed to proceed for up to 48 hours and it was observed that the viscosity became rather high after 24 hours. In view of the reaction kinetics discussed earlier, it seems probable that most of the piperazine first reacts with the diglycidyl ether and later, the piperazine capped diglycidyl ether further reacts with the epoxy functional siloxane to produce a linear copolymer. In any event, it was possible to make a reaction product after 48 hours and to cast clear transparent films that adhered very strongly to glass surfaces. Further work on these segmented linear polyhydroxyether siloxane copolymers is continuing. Indeed, such materials may be of interest in their own right as novel adhesives.

Scheme 11




## CONCLUSIONS

Functional siloxane oligomers bearing either epoxy, aminopropyl, hydroxy piperazine or piperazine endgroups were

synthesized via equilibration polymerization of the cyclic tetramer and the appropriate disiloxane. The reactions were further characterized by spectroscopic analysis and in some cases gel permeation chromatography. Incorporation of the siloxanes into epoxy networks was investigated. The behavior of the resulting networks was highly dependent upon the nature of the functional endgroup. The reactivity of the epoxy functional siloxane systems was very slow relative to the curing reaction and hence, epoxy functional siloxanes produced undesirable, turbid, incompatible films. Aminopropyl terminated modifiers also produced inhomogeneous networks. Only networks prepared with the secondary amine terminated systems, e.g. piperazine functionality, were able to produce homogeneous cured networks. Networks of starting material disiloxanes were also investigated and in those cases it was possible to produce transparent somewhat tough films. However, the glass temperature was reduced by the short siloxane material. Oligomeric species up to 5000 molecular weight, however, did not significantly depress the glass temperature of the network from its control value of about 150°C. Surface modification of the epoxy networks was studied by both ESCA spectroscopy and ATR-FTIR methods. In both cases, it could be demonstrated that piperazine capped oligomers were able to significantly enrich the surface with siloxane structures.

## FUTURE WORK

We have at this point generated functional oligomers that can be quantitatively incorporated into epoxy networks. It is clear that surface modification is possible by this method. Our future work is focusing on the mechanical property behavior of these modified siloxane systems. In particular, we are investigating the morphology and structure of the dispersed phase as a function of siloxane concentration and block length. Stress strain properties at low extension rates as well as impact studies using our recently designed impact tester are being pursued (22).

## Acknowledgement

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## Figure Captions

Figure 1. Effect of Catalyst Concentration on Epoxy Terminated Polydimethylsiloxane Equilibrations (44 hrs. reaction time)

Figure 2. Effect of Reaction Time on Epoxy Terminated Polydimethylsiloxane Equilibrations (0.5% wt. Catalyst)

Figure 3. Comparison of Percent Conversion-Temperature Behavior of Various Siloxane Modified Epoxy-Amine Systems. Dynamic DSC Scans with a Heating Rate of 10°C/Minute.

(1) o EPON Resin-828 + Piperazine Capped Siloxane Dimer (DSX)

(2) ▲ EPON Resin-828 + Aminopropyl Terminated DSX

(3) Δ EPON Resin-828 + PACM-20

(4) ■ Epoxy Terminated DSX + PACM-20

Figure 4. Comparison of Reactivity Isothermal Reaction Rates (Reactivities) of Various SIloxane Modifiers with EPON Resin-828 at 100°C.

(1) o EPON Resin-828 + Piperazine Capped Siloxane Dimer (DSX) (at 80°C)

(2) ▲ EPON Resin-828 + Aminopropyl Terminated DSX

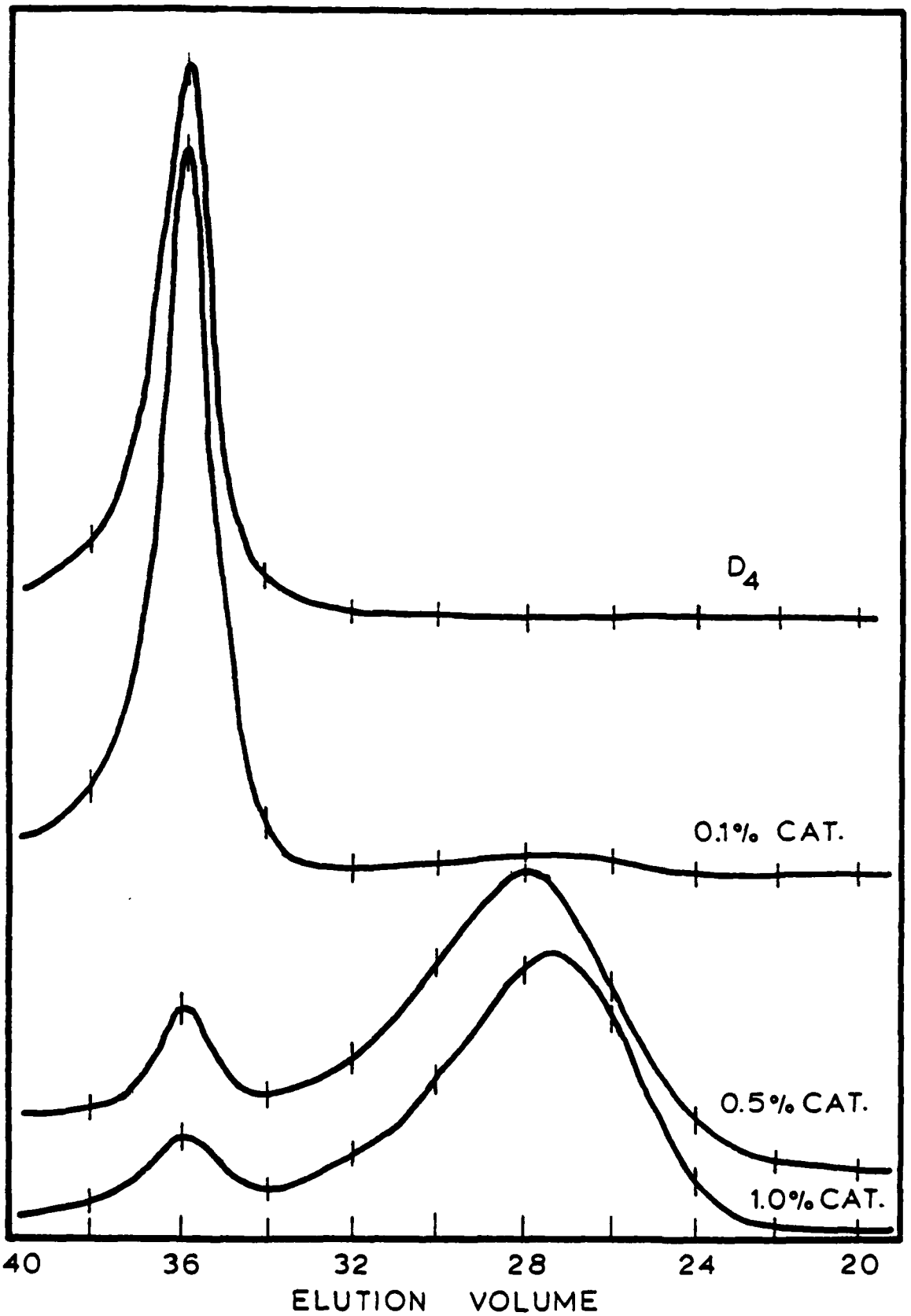
(3) Δ EPON Resin-828 + PACM-20

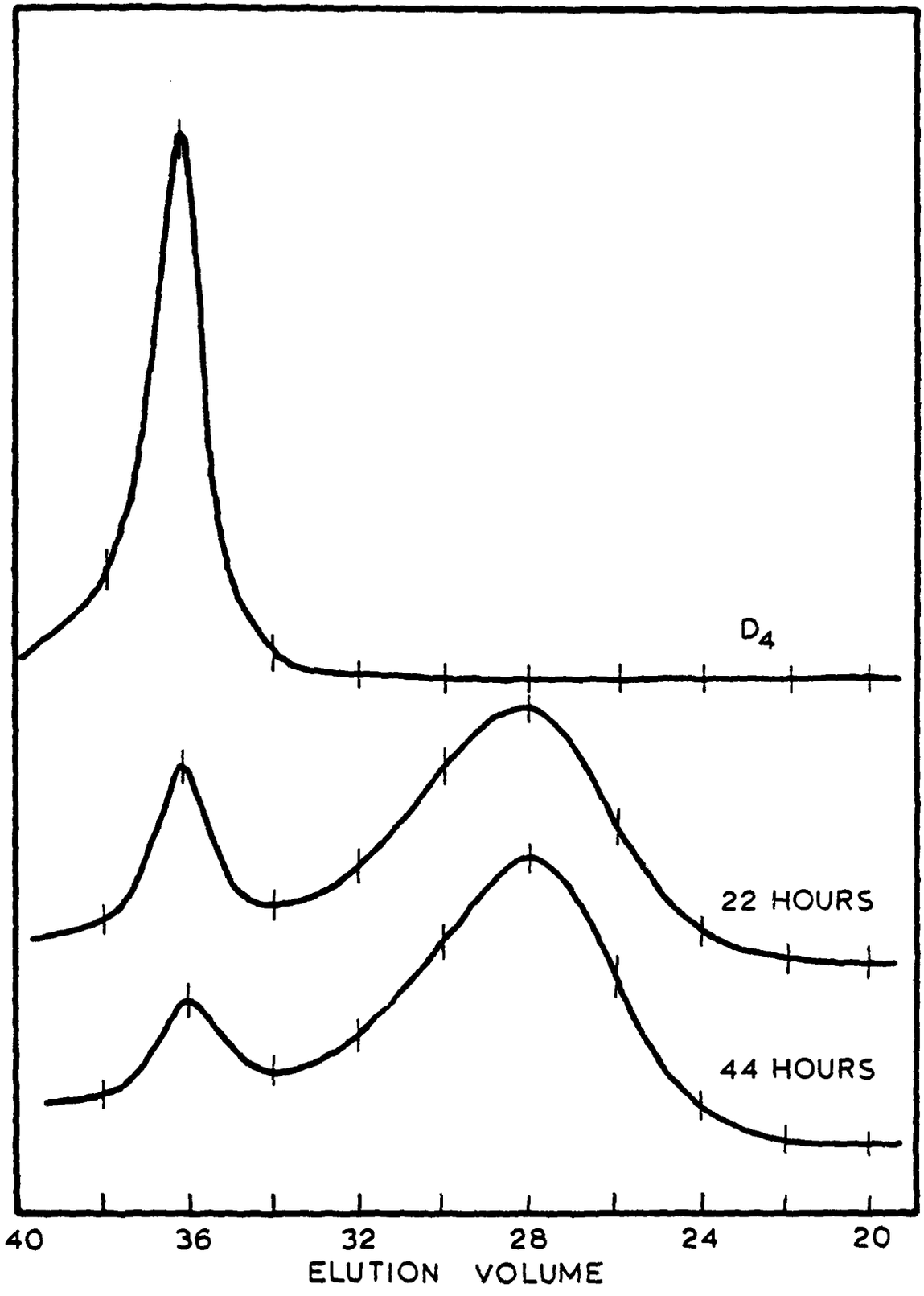
(4) ■ Epoxy Terminated DSX + PACM-20

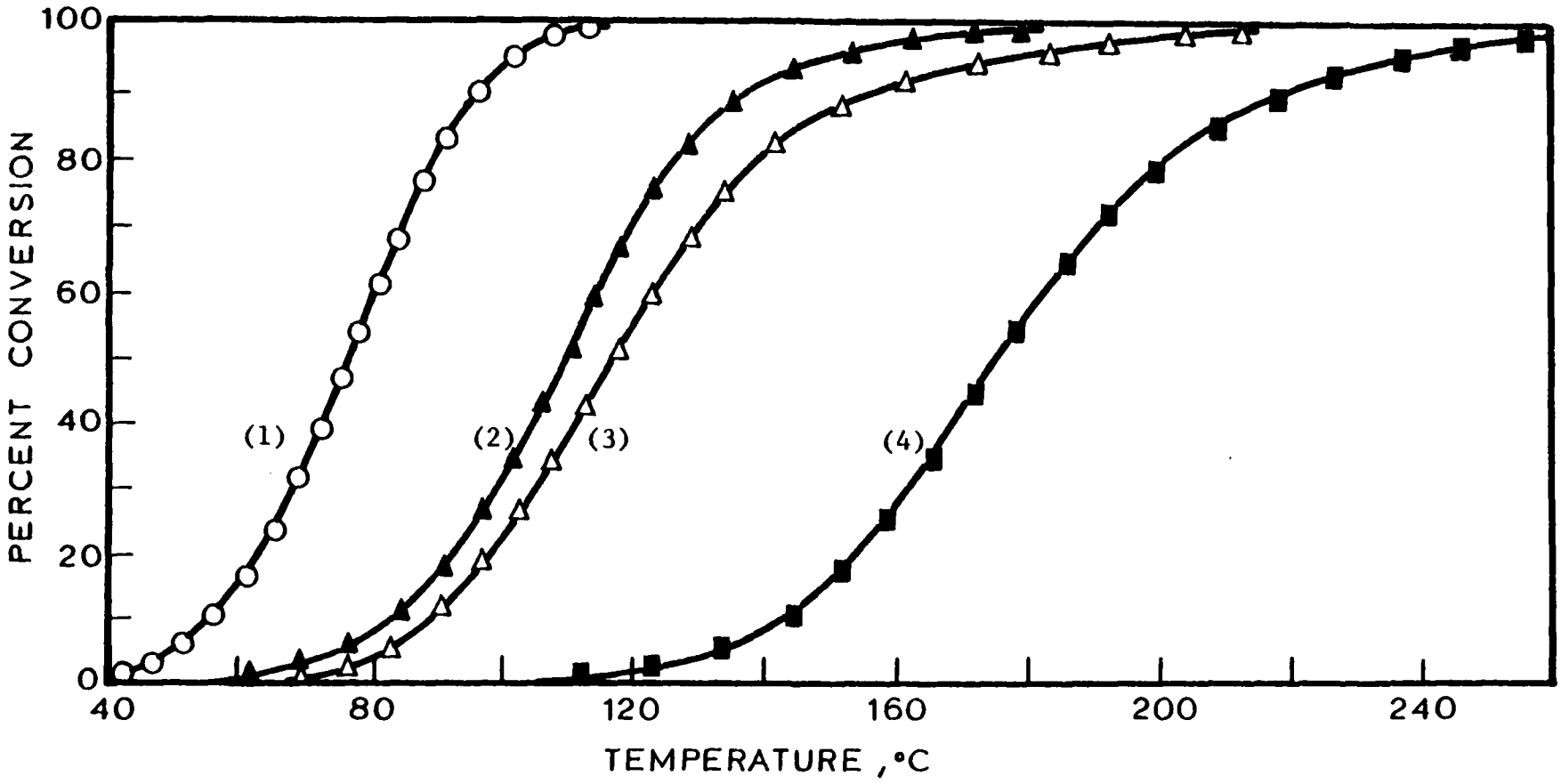
(5) ● EPON Resin-828 + Piperazine Capped PSX ($\overline{M}n$=4200)

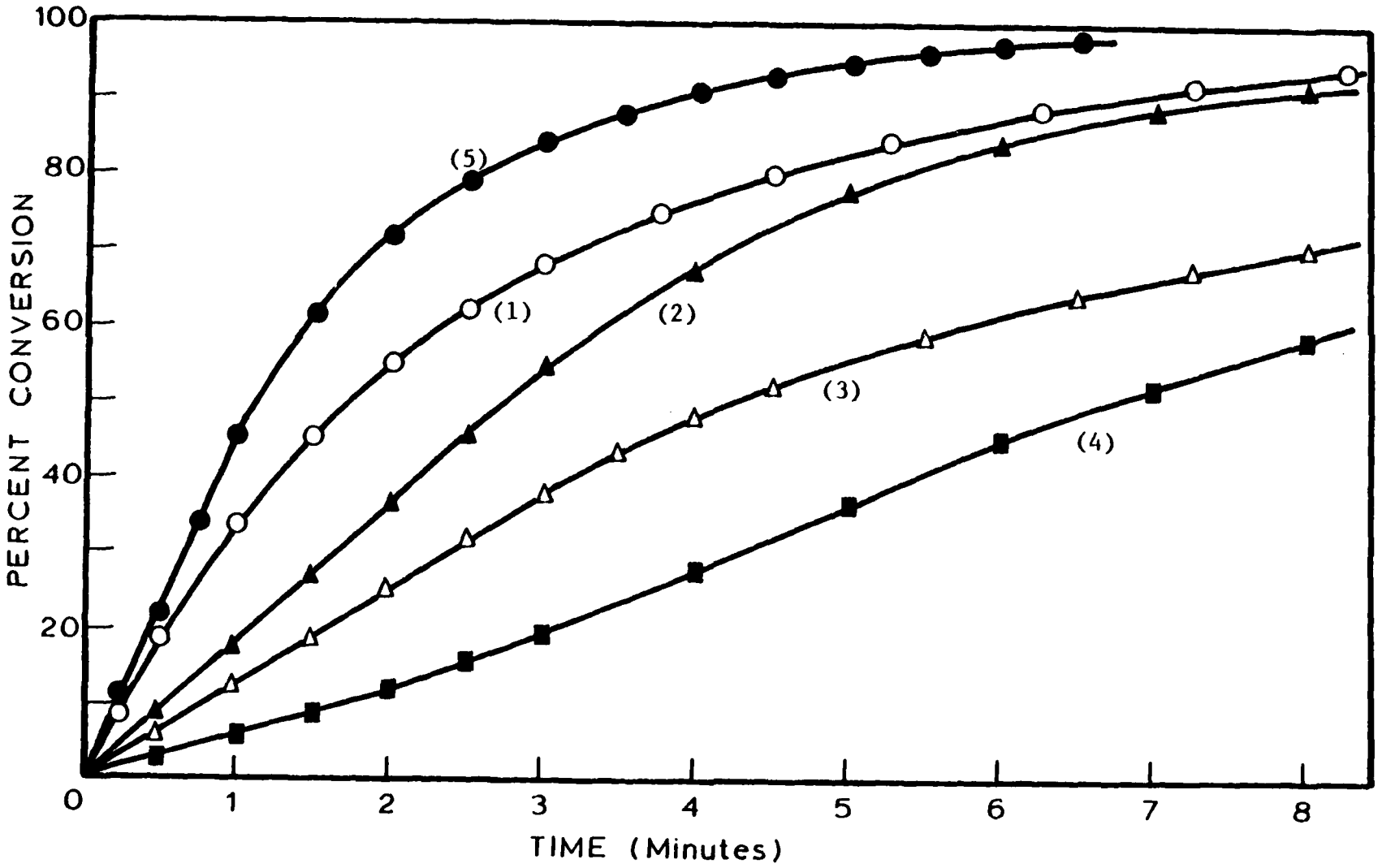
Figure 5. ATR/FTIR Spectrum of 2% Piperazine Terminated Siloxane Dimer-Modified Epoxy Networks

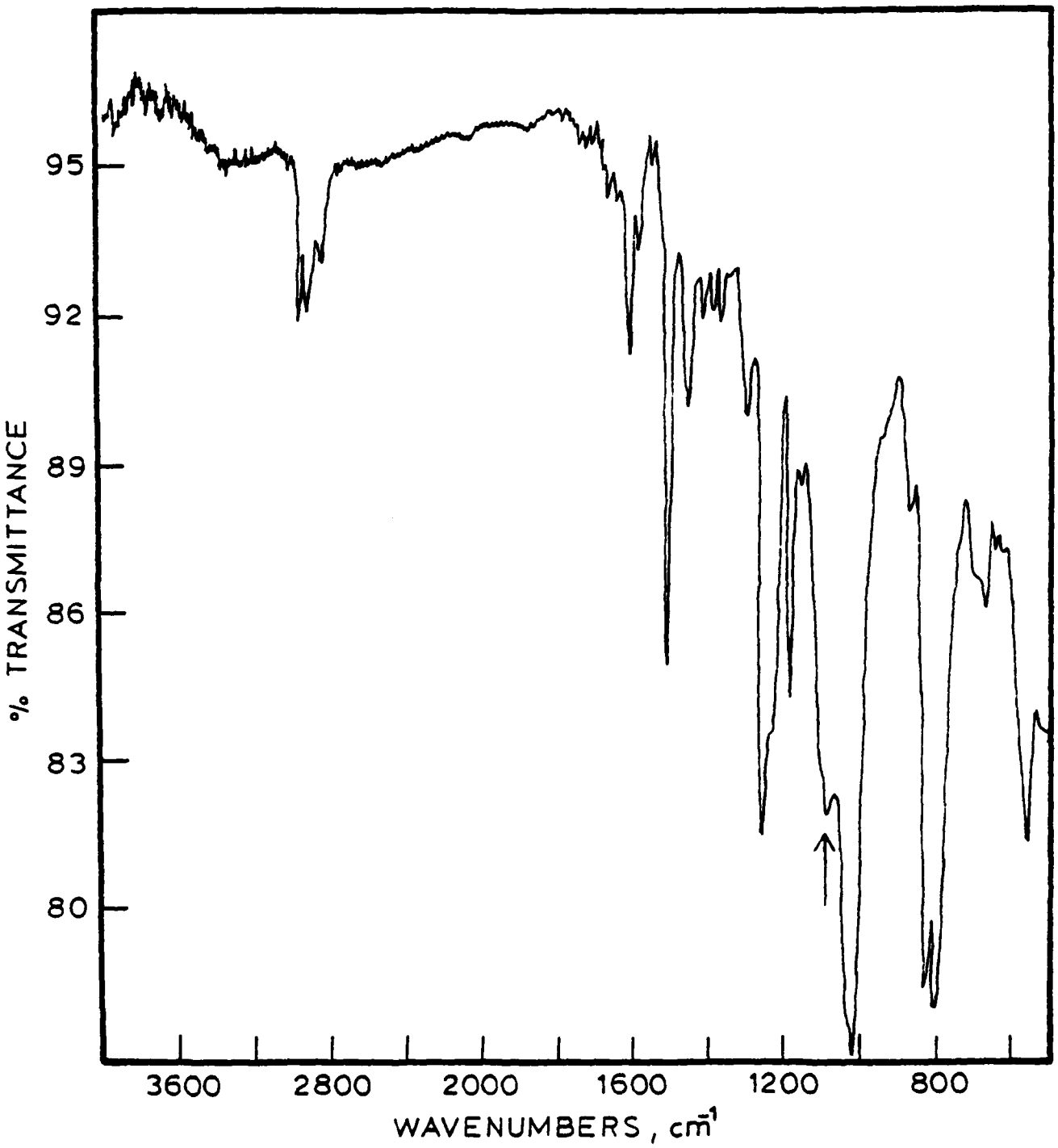
Figure 6. ATR/FTIR Spectrum of 2% Piperazine Terminated Siloxane Oligomer Modified Epoxy Networks (Mn = 4200)

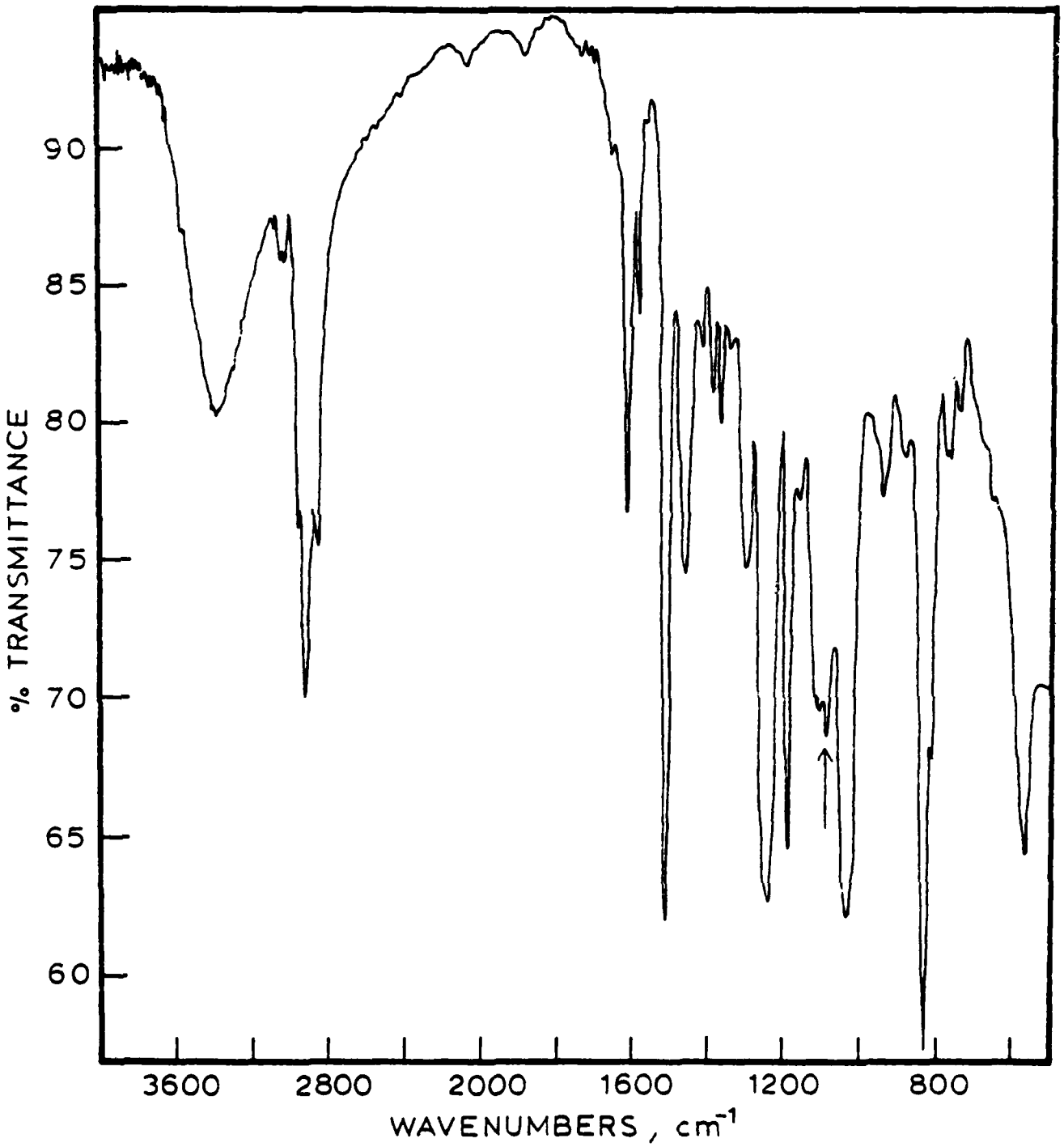

D4
0.1% CAT.
0.5% CAT.
1.0% CAT.
40
36
32
28
24
20
ELUTION VOLUME


D4
22 HOURS
44 HOURS
40
36
32
28
24
20
ELUTION VOLUME


PERCENT CONVERSION
100
80
60
40
20
0
40
80
120
160
200
240
TEMPERATURE ,°C
(1)
(2)
(3)
(4)


100
80
60
40
20
0
PERCENT CONVERSION
1
2
3
4
5
6
7
8
TIME (Minutes)
(5)
(1)
(2)
(3)
(4)


95
92
89
86
83
80
% TRANSMITTANCE
3600
2800
2000
1600
1200
800
WAVENUMBERS, cm⁻¹


% TRANSMITTANCE
90
85
80
75
70
65
60
3600
2800
2000
1600
1200
800
WAVENUMBERS , cm⁻¹

END

FILMED

6-83

DTIC